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Tip-enhanced fluorescence imaging of quantum dots

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We have imaged the fluorescence from a single quantum dot cluster using an apertureless scanning near-field optical microscope. When a sharp gold tip is brought within a few nanometers from the sample surface, the resulting enhancement in quantum dot fluorescence in the vicinity of the tip leads to a resolution of about 60 nm. We determine this enhancement of the fluorescence to be about fourfold in magnitude, which is consistent with the value expected as a result of competition between fluorescence quenching and electromagnetic field enhancement. © 2005 American Institute of Physics. [DOI: 10.1063/1.2115073]

Optical imaging with resolutions below the diffraction limit is made possible by the technique of scanning near-field optical microscopy (SNOM).^{1–3} In its standard implementation, light is collected or illuminated through a subwavelength aperture at the end of a metal-coated optical fiber. However, the rapidly decreasing light throughput with decreasing aperture diameter confines the practical resolution limit of this technique to ~ 50 nm.¹ Higher optical resolution can potentially be achieved with “apertureless” scanning near-field optical microscopy (ASNOM), in which a sharp tip is used to locally increase the electric field illuminating a sample surface.^{2,3} The nano-optical field in the vicinity of the tip apex is strongly enhanced due to both the resonant excitation of localized surface plasmons and the lightning rod effect of highly curved metal surfaces. High resolution Raman imaging on isolated single wall carbon nanotubes⁴ and subwavelength resolution optical imaging of fluorescence molecules⁵ and quantum dots^{6,7} has been reported.

For fluorescence ASNOM, there are many ways in which a sharp metallic tip can affect the fluorescence of nearby molecules.⁸ In addition to an enhancement in fluorescence signal from the enhancement of the local electromagnetic field,^{5–7,9} placing a sharp metallic tip in the vicinity of a fluorescence molecule also leads to a modification of both the radiative and the nonradiative rate for a molecule, inducing changes in both the fluorescence lifetime and the emission intensity.^{8,10} The measured fluorescence enhancement in an ASNOM image will be the result of a combination of these effects; whether an enhanced or a quenched fluorescence intensity is observed depends strongly on the particular experimental conditions. Experimentally, both fluorescence intensity enhancement^{5–7,9} and fluorescence intensity quenching^{5,11} have been reported.

Additional insight about the interplay between these effects can be obtained from a calculation of the expected fluorescence enhancement in ASNOM, employing a simple static model following the approach described by Metiu.¹² The tip is modeled as a sphere of radius $r=30$ nm (using the bulk dielectric constant for gold¹³ for excitation and emission wavelengths of, respectively, 514 and 640 nm) and the fluorescent molecule as a dipole located at a distance d from the surface of the sphere [see the inset of Fig. 1(a)]. Figure 1(a)

shows the expected fluorescence enhancement factor as a function of sphere-dipole (i.e., tip-sample) separation d , with the contributions from the electromagnetic field enhancement and of the fluorescence quenching induced by the gold sphere also indicated. The total enhancement is the product of these two contributions. The quenching is given by the ratio of the lifetime modified by the gold sphere and the lifetime of a free molecule. We can see that when the dipole is far from the sphere surface ($d > 20$ nm), quenching is negligible and electromagnetic field enhancement dominates, while quenching dominates for separations $d < 5$ nm. A maximum signal enhancement of ~ 5 is predicted for a separation of ~ 17 nm, with an enhancement greater than 3 for tip-sample separations between 10 and 40 nm.

In this letter, we present ASNOM fluorescence measurements of an isolated small cluster of CdSe(ZnS) core-shell quantum dots (QDs) (Quantum Dot Corporation) with an emission wavelength of 640 nm. The QD diameter is 2–3 nm while the overall size, including polymer coating, is 15–20 nm. A solution of QDs in a phosphate buffer was further diluted in water and dropped onto a clean glass coverslip, followed by air drying, to create a disperse film of QDs. Wide-field fluorescence imaging indicated QD emission from points with a typical separation of a few microns. The observation of fluorescence blinking, a characteristic feature of single QDs,¹⁴ confirmed that these fluorescence

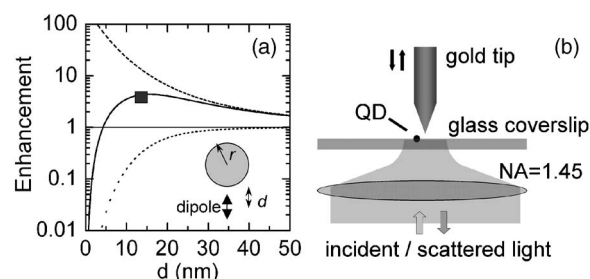


FIG. 1. (a) Calculated fluorescence enhancement (solid line) for a molecule or quantum dot nanoparticle a distance d from a gold tip, using a simple model depicted in the inset and following the approach of Ref. 12. Contributions from electromagnetic field enhancement (dashed line) and quenching (dotted line) are also shown. The data point determined from our measurements is also indicated. (b) Schematic diagram of the experiment: A sharp Au tip is positioned at the center of the laser focus with tip-sample separation controlled by shear-force feedback. Confocal fluorescence and topography images are obtained simultaneously as quantum dots are scanned through the focus.

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sources comprised one or at most a small number of QDs, and enabled an easy differentiation from larger aggregates and fluorescent impurities. QDs in very low density samples were found to exhibit blinking rates with much lower on/off time ratios to those observed in the present sample under similar excitation conditions. This suggests that the low-density films are comprised of isolated single QDs, whereas higher-density samples, such as those considered here, contain a disperse film of small clusters of QDs.

Our experimental setup [Fig. 1(b)] is based on an inverted confocal optical microscope in which the incident light ($\sim 3 \mu\text{W}$ at 514 nm) is illuminated with an oil immersion lens with a high numerical aperture (NA1.45, Nikon 100X) and focused to a diffraction-limited spot on the sample surface. The use of this high NA lens leads to some total internal reflection at the glass-air interface, producing a strong evanescent field component at the sample surface. The same lens is also used to collect the fluorescence, which is filtered by a 520-nm edge filter and a bandpass filter (centered at 650 nm with 40 nm FWHM) and coupled to a multimode optical fiber for confocal detection.

Tips were prepared by electrochemically etching a gold wire (0.1 mm diam) in HCl acid (20%). In topographic images we routinely observe feature sizes that suggest the typical tip radius is ~ 30 nm. We acquire our images by scanning the sample laterally while moving the tip vertically under shear force feedback,¹ which allows reliable positioning of the tip apex within 1–2 nm of the sample surface. The use of an axially rigid probe and shear-force feedback provides the advantage, over normal-force feedback using a cantilever, of a constant tip-sample separation, which was held at 5 nm in the present experiments. The position of the tip in the laser focus is optimized by maximizing the intensity of the broadband emission continuum¹⁵ from the illuminated gold tip, which is observed when no QDs are within the laser focus.

Figure 2(a) shows a $1 \mu\text{m} \times 1 \mu\text{m}$ fluorescence confocal image of a single QD cluster with no tip present. We can clearly observe in the image intensity fluctuations due to the fluorescence blinking.¹⁴ The resolution in Fig. 2(a) is about 200 nm (as indicated by the line profile in Fig. 2(d) of a scan line in which no blinking event occurred), consistent with the size of the diffraction-limited focus. A gold tip was then brought within 5 nm of the sample surface, using shear-force feedback, and the same $1 \mu\text{m} \times 1 \mu\text{m}$ area was scanned again while recording simultaneously both fluorescence intensity [Fig. 2(b)] and topography [Fig. 2(c)]. The step size in both the confocal [Fig. 2(a)] and ASNM [Figs. 2(b) and 2(c)] scans was 30 nm, with each pixel in the images of Fig. 2 representing a scan point. The central feature of the ASNM image [Fig. 2(b)] is at the same position as the image of the QD cluster observed in the confocal scan [Fig. 2(a)]. From a comparison of these images we can observe a dramatic improvement in the spatial resolution of the fluorescence image when the gold tip is in close proximity to the sample surface. The full width at half maximum (FWHM) of the ASNM image of the QD cluster is 60 nm [see Fig. 2(e)], considerably smaller than that of the diffraction-limited FWHM observed in the confocal image [Fig. 2(d)].

The QD cluster is readily apparent in the center of the topographic image [Fig. 2(c)], correlating with the center of fluorescence images of the QD cluster. The height of the QD cluster is ~ 15 nm [see Fig. 2(f)], in good agreement with the diameter of a single QD. This, combined with the observa-

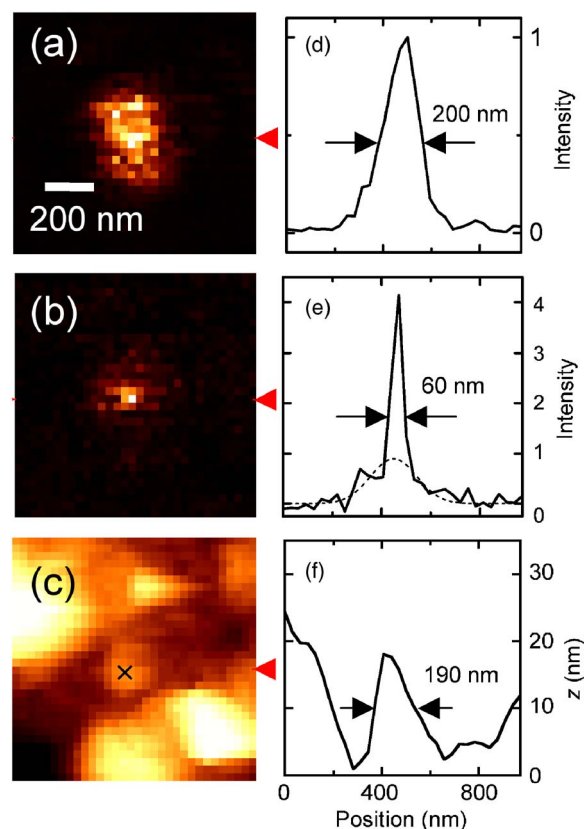


FIG. 2. (Color online). $1 \mu\text{m} \times 1 \mu\text{m}$ (a) fluorescence confocal (no tip), (b) fluorescence ASNM and (c) topographic images of a single CdSe/ZnS quantum dot cluster. (b) and (c) obtained simultaneously with a sharp Au tip close at the center of the laser focus. The cross in (c) indicates the nanoparticle. (d) Fluorescence confocal, (e) fluorescence ASNM, and (f) topographic line profiles, along the scan lines indicated by the red arrows in (a), (b), and (c), respectively. The fluorescence signals in (d) and (e) are normalized to the diffraction-limited signal in both scans; a fit to the diffraction-limited signal is indicated by the dashed line in (e).

tion of fluorescence blinking in the confocal fluorescence image, allows us to confirm that the measured images are from a cluster of only a few QDs. In Fig. 2(c) we can also observe a number of features, which do not appear in the fluorescence images, and probably result from residues of the initial QD buffer solution or air contamination. It is likely that the cluster is also surrounded by such nonfluorescent material, resulting in the large apparent 190-nm lateral extent of the cluster in the topographic image.

Closer inspection of the ASNM image [Fig. 2(b)] indicates that the strong sharp peak sits on a weak blinking background signal with diffraction limited size. The line profile in Fig. 2(e) demonstrates this clearly, as does a vertical line profile (along the slow scan direction), indicating in particular that the strong central feature is symmetric (it should be noted that those pixels surrounding the central bright pixel also contribute to this central region of enhanced fluorescence). Indeed, it appears that the QD blinking is reduced significantly when the distance between the tip and the QDs is reduced to a few tens of nanometers. This seems consistent with the results of Shimizu *et al.*, who observed a fivefold enhancement of the fluorescence intensity and a striking reduction in the fluorescence blinking of CdSe(ZnS) QDs adsorbed on a rough gold surface.¹⁶

Some photobleaching of the QD cluster between scans prevents a direct comparison between the peak intensities observed in Figs. 2(a) and 2(b). Instead, the line profiles in Figs. 2(d) and 2(e) are normalized to the diffraction-limited signals in the confocal and ASNO images (note that QD blinking introduces some uncertainty in analysis of the diffraction-limited signal). By calculating the ratio between the peak intensities of the sharp subdiffraction peak and the diffraction-limited background in Fig. 2(b), we determine an enhancement in the fluorescence signal of 4 ± 1 when the gold tip is directly over the QD cluster. At this point the QD-tip separation is 12–15 nm (a combination of the 5-nm tip-sample separation and the 7–10-nm polymer shell on the QD nanoparticles). This is in excellent agreement with our simple calculation of the fluorescent enhancement [Fig. 1(a)].

In summary, we report fluorescence imaging with a resolution of 60 nm, on a small CdSe quantum dot cluster using tip-enhanced ASNO. The enhancement of the fluorescence signal is about fourfold in magnitude. This is in good agreement with a simple model for the effect of the tip, and results from a competition between the enhancement of the local field and quenching of the fluorescence by the gold tip. We conclude that, for a gold tip and illumination conditions similar to those employed here, a tip-surface separation of 10–15 nm is required in fluorescence ASNO for both optimal tip-enhancement and resolution.

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